

(11) **EP 1 122 506 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 158(3) EPC

(43) Date of publication:
08.08.2001 Bulletin 2001/32

(51) Int Cl.7: **F28F 19/02, F28F 21/00,
F28F 21/04, F28F 21/08,
F28F 1/12**

(21) Application number: **00949969.0**

(86) International application number:
PCT/JP00/05205

(22) Date of filing: **03.08.2000**

(87) International publication number:
WO 01/13057 (22.02.2001 Gazette 2001/08)

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE**
Designated Extension States:
AL LT LV MK RO SI

(72) Inventors:
• **3NOTO, Takashi, NKK Corp.**
Tokyo 100-0005 (JP)
• **NISHIO, Hiroaki, NKK Corp.**
Tokyo 100-0005 (JP)

(30) Priority: **12.08.1999 JP 22858999**
12.08.1999 JP 22859099
12.08.1999 JP 22859199
12.08.1999 JP 22859299

(74) Representative: **HOFFMANN - EITLE**
Patent- und Rechtsanwälte
Arabellastrasse 4
81925 München (DE)

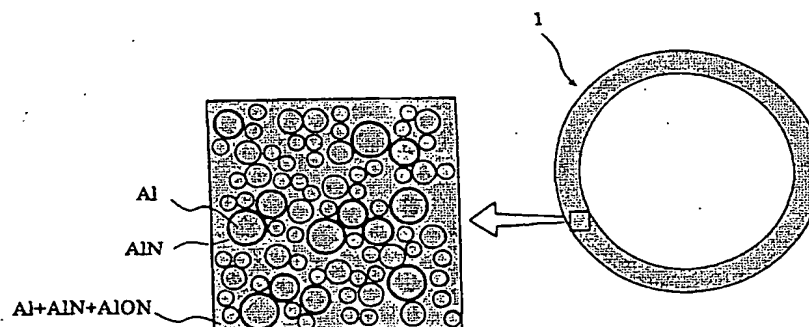
(71) Applicant: **NKK CORPORATION**
Tokyo 100-0005 (JP)

(54) **HEAT EXCHANGE TUBE AND HEAT RECOVERY METHOD USING IT**

(57) The present invention relates to a heat exchanger tube made of a sintered compact having pore ratio of 2 to 60%, a heat exchanger tube wherein the outer part thereof is made of a ceramics metal composite, more preferably, a heat exchanger tube wherein a heat resisting alloy tube is covered with a ceramics metal composite in non adhesive condition, and the heat

resisting alloy tube and the ceramics metal composite at least partly contact at the interface therebetween. By means of the heat exchanger tubes of the present invention, stable heat recovery can be carried out for a long period of time even under corrosive environment at high temperature such as in a combustion waste gas of industrial waste.

FIG. 1



Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention relates to a heat exchanger tube for heat recovery through steam or air from a waste gas at high temperature occurring when burning municipal waste or industrial waste, and to a heat recovery method using the same.

2. Description of Related Art

[0002] Nowadays, a heat recovery system has been reduced to practice for recovering heat through a heat exchanger tube where heat exchanger fluids such as steam or air flow from the waste gas at 400 to 1200° C generated by burning municipal waste, coal, sewage, paper making sludge or other industrial waste. And the recovered heat is used, for example, for power generation.

[0003] But since the waste gas generated when burning municipal waste or industrial waste, contains hydrogen chloride and basic salt such as NaCl, KCl or Na₂SO₄ having corrosivity stronger as a temperature becomes higher, the heat exchanger tubes made of heat resisting alloys such as boiler carbon steel or alloy steel, stainless steel or Ni-Co alloy, can not be used under conditions at high temperature, and the temperature of heat exchanger fluid passing within the heat exchanger tube is controlled to be 300° C or lower. Actually, the heat recovery has not sufficiently been carried out.

[0004] For enabling to recover heat at higher temperature without causing corrosion, Japanese Patent Laid-Open No.332508(1993) proposes a heat exchanger made of a ceramics, and Japanese Patent Laid-Open No.274401(1998) proposes a heat exchanger made of a heat resisting alloy covered with a ceramics film.

[0005] However, being exposed to corrosive environment at high temperature for a long period of time, the ceramics is caused with cracks or peeling due to the difference in coefficient of thermal expansion between the ceramics and the deposit of ash containing basic salt adhered or deposited on the ceramics surface, or due to the difference in coefficient of thermal expansion between the ceramics and the heat resisting alloy, so that the stable heat recovery cannot be secured for a long time. Further, the ash deposit becoming thicker decreases heat transfer coefficient, and invites degradation of heat exchanger effectiveness.

SUMMARY OF THE INVENTION

[0006] It is accordingly an object of the present invention to provide a heat exchanger tube enabling to carry out stable heat recovery for a long time even under corrosive environment at high temperature, and a heat re-

covery method using the same.

[0007] This object is accomplished by means of a heat exchanger tube made of a sintered compact having pore ratio of 2 to 60%, or a heat exchanger tube wherein the outer part thereof is made of a ceramics metal composite.

[0008] In particular, the heat exchanger tube is more preferable, wherein a heat resisting alloy tube is covered with a ceramics metal composite in non adhesive condition, and the heat resisting alloy tube and the ceramics metal composite at least partly contact at the interface therebetween, or a heat exchanger tube wherein a heat resisting alloy tube is covered in succession with a thermal expansion buffer and a ceramics metal composite in non adhesive condition, and both at least partly contact at the interface between the heat resisting alloy tube and the thermal expansion buffer and/or at the interface between the thermal expansion buffer and the ceramics metal composite.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009]

Fig. 1 is a vertically cross sectional view of the heat exchanger tube as one example of the invention; Fig. 2 is a vertically cross sectional view of the heat exchanger tube as another example of the invention;

Fig. 3 is a laterally cross sectional view of the heat exchanger tube as another example of the invention;

Fig. 4 is a vertically cross sectional view of the heat exchanger tube as another example of the invention;

Fig. 5 is a laterally cross sectional view of the heat exchanger tube of Fig. 4;

Fig. 6 is a laterally cross sectional view of the heat exchanger tube as another example of the invention;

Fig. 7 is a laterally cross sectional view of the heat exchanger tube as another example of the invention;

Fig. 8 is a vertically cross sectional view of the heat exchanger tube as another example of the invention;

Fig. 9 is a laterally cross sectional view of the heat exchanger tube of Fig. 8;

Fig. 10 is a laterally cross sectional view of the heat exchanger tube as another example of the invention; and

Fig. 11 is a laterally cross sectional view of the heat exchanger tube as another example of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0010] In order to obtain a heat exchanger tube that

can be steadily served for a long time under corrosive environment at high temperature, we made studies from the following two points of view, how to prevent the deposition of ash and how to suppress the crack of ceramics itself.

[0011] AS a result, it is found that if realizing such a heat exchanger tube made of a sintered compact of metal or ceramics having pore ratio of 2 to 60%, the deposition of ash containing basic salt can be prevented by spouting a part of heat exchanger fluid passing within the heat exchanger tube through the pores. In this case, if the pore ratio thereof is 2% or more, a production process under special circumstance at high temperature and high pressure is not necessary and the production cost is lowered. If the pore ratio is not less than 60%, highly corrosive waste gas penetrates from the pores and degenerates the tube itself. As a method for spouting a part of heat exchanger fluid through the pores, it is simply sufficient to strengthen the pressure of the heat exchanger fluid flowing in the heat exchanger tube to be higher than the pressure of atmosphere outside of the heat exchanger tube.

[0012] It is preferable that the heat exchanger tube should be made of a sintered compact of ceramics metal composite, because the excellent corrosion resistance is achieved by the ceramics, and at the same time the ductility is improved by the metal.

[0013] On the other hand, it is effective that the outer part of heat exchanger tube is made of a ceramics metal composite so as to suppress the crack of ceramics itself for the same reason as described above.

[0014] As a ceramics in the ceramics metal composite, available are oxides such as TiO_2 , ZrO_2 , Cr_2O_3 , Al_2O_3 , SiO_2 , Y_2O_3 , CeO_2 , Sc_2O_3 , borides such as BN, MgB_2 , CaB_6 , TiB_2 , ZrB_2 , AlB_2 , carbides such as B_4C , TiC , ZrC , Cr_3C_2 , Al_4C_3 , SiC , nitrides such as AlN , TiN , ZrN , Cr_2N , Si_3N_4 , and oxide-nitrides such as AlON , $\text{Si}_2\text{N}_2\text{O}$, or their compounds.

[0015] As a metal in the ceramics metal composite, any metals may be employed, but preferable are Al, Al-Si alloy or Al-Mg alloy which are superior in heat conductivity and advantageous in cost.

[0016] If Al is contained in the ceramics metal composite, it is more preferable to contain AlN as a ceramics which is excellent in the thermal shock resistance and hard to catch ash. Moreover, it is easier to fabricate an Al+ AlN composite because of being sufficient with only heat-treating Al in an N_2 atmosphere during processing. In this case, for suppressing the occurrence of corrosion or crack under corrosive environment at high temperature, AlN should be 1 to 90wt% and Al+ AlN be 50wt% or higher.

[0017] If AlON is further added to the ceramics metal composite containing AlN as a ceramics and Al as a metal, the ash is harder to adhere to the heat exchanger tube. In this case, AlN should be 1 to 90wt% and Al+ AlN + AlON be 50wt% or higher. Herein, AlON is defined as a general term of compound of Al, O, N, and

shows $\text{Al}_{11}\text{O}_{16}\text{N}$, AlON , $\text{Al}_{198}\text{O}_{288}\text{N}_4$, $\text{Al}_{27}\text{O}_{39}\text{N}$, $\text{Al}_{10}\text{O}_3\text{N}_8$, $\text{Al}_3\text{O}_3\text{N}_7$, $\text{SiAl}_7\text{O}_2\text{N}_7$, $\text{Si}_3\text{Al}_3\text{O}_{4.5}\text{N}_5$ and the like.

[0018] When compounds containing B as BN or B_4C , or C as SiC or graphite are caused to exist by spraying or immersing with a thickness, for example, of 1 to 400 μm , on the surface of the ceramics metal composite, the ash is almost completely prevented from adherence thereto. Further, the spraying or immersion of the compound is carried out periodically, whereby the heat exchanger tube can be stably used for a longer time.

[0019] It is possible that the heat exchanger tube is composed of an outer part made of this ceramics metal composite and an inner part made of an existing heat resisting alloy tube. The thickness of the ceramics metal composite part is then preferably 3 to 12mm from the viewpoint of strength.

[0020] If such a structure is provided where a heat resisting alloy tube is covered with a ceramics metal composite in non adhesive condition, the thermal strain is moderated due to the difference in coefficient of thermal expansion in an axial direction of tube between the heat resisting alloy and the ceramics metal composite, thereby enabling to more reliably avoid the occurrences of cracks or peeling of the ceramics metal composite. In addition, if the heat resisting alloy tube and the ceramics metal composite at least partly contact at the interface therebetween, the heat transfer coefficient does not largely go down but the heat recovery can be done at high heat exchanger effectiveness.

[0021] The ceramics metal composite in this case should preferably contain AlN of 1 to 90wt% and Al+ AlN + AlON of 50wt% or higher, and have pore ratio of 2 to 60% for the above mentioned reason.

[0022] If the compound containing B or C as said above exists on the outer surface of the heat resisting alloy tube, the contacting part between the heat resisting alloy and the ceramics metal composite smoothly slides, and the thermal strain due to the difference in the coefficient of thermal expansion is almost perfectly relieved.

[0023] If such a structure is provided where a heat resisting alloy tube is covered in succession with a thermal expansion buffer and a ceramics metal composite in non adhesive condition, and both at least partly contact at the interface between the heat resisting alloy tube and the thermal expansion buffer and/or at the interface between the thermal expansion buffer and the ceramics metal composite, the thermal strain due to the difference in the coefficient of thermal expansion is almost relieved not only in an axial direction of tube but in a radial direction of tube due to the thermal expansion buffer.

[0024] Herein, it is possible to employ, as a thermal expansion buffer, materials such as fiber, powder, film or tape containing B, C or Al as main elements.

[0025] Similarly to the case that the heat exchanger tube is composed of an outer part made of ceramics metal composite, the ceramics metal composite should preferably contain AlN of 1 to 90wt% and Al+ AlN + AlON

of 50wt% or higher, and have pore ratio of 2 to 60%. In addition, preferably the compound containing B or C exists on the outer surface of the heat resisting alloy tube.

[0026] In any of the above mentioned heat exchanger tubes, taking the cracks of sintered compact or ceramics metal composite, the strength or the heat transfer of heat exchanger tube itself into consideration, it is preferable that the tube length is 6mm or shorter and the tube outer diameter is 20 to 200mm. The cross sectional shape is sufficient with circle or rectangle, not particularly limiting.

Example 1

[0027] There were installed for heat recovery, in the waste gas at high temperature of 750 to 950° C of a municipal waste combustion pilot plant, the heat exchanger tube No. 1 of single layer structure made of a ceramics metal composite 1 having a vertically cross sectional shape and a microstructure shown in Fig. 1, the heat exchanger tube No. 2 of three layer structure having a vertically cross sectional shape shown in Fig. 2 where the first layer was a heat resisting alloy tube 2, the second layer was a carbon fiber 3, and the third outer layer was a ceramics metal composite 1, and the heat exchanger tube No. 3 coated with BN on the outer surface of the heat exchanger tube No. 2.

[0028] The details of the heat exchanger tubes Nos. 1 and 2 are as follows.

Heat exchanger tube No. 1

[0029] Ceramics metal composite: Al+AlN+AlON of 90wt% or higher, thickness of 4mm, outer diameter of 40mm.

Heat exchanger tube No. 2

[0030] Heat resisting alloy tube: SUS304, thickness of 4mm, Carbon fiber: thickness of 4mm, Ceramics metal composite: Al+AlN+AlON of 90wt% or higher, thickness of 10mm, outer diameter of 40mm.

[0031] The component of the waste gas of the municipal waste combustion pilot plant was O₂ of 2 to 16% (vol and dry are the same in the following), HCl of 100 to 500ppm, SO_x of max 300ppm, CO₂ of 5 to 18% and the rest being N₂. The heat exchanger fluid flowing in the heat exchanger tube was steam of 150 to 400° C at the inlet, and mixed gas of 120 to 300° C at the inlet of air and combustion waste gas.

[0032] As a result, it was confirmed that in each of the heat exchanger tubes, the reduction amount of thickness by corrosion was slight, no crack occurred, and the stable heat recovery was possible for a long time. In particular, in the BN-coated heat exchanger tube No. 3, the reduction amount of thickness by corrosion was 30% or lower of that of the heat exchanger tubes Nos. 1 and 2.

Example 2

[0033] The heat exchanger tubes Nos. 4 and 5 of single layer structure made of a ceramics metal composite 1 having a vertically cross sectional shape and pores 4 shown in Fig. 3 were installed for heat recovery in the waste gas at high temperature of 750 to 950° C of the municipal waste combustion pilot plant similarly to Example 1, and the pressure of the heat exchanger fluid was strengthened than the pressure of the waste gas atmosphere for a part of the heat exchanger fluid to be spouted from the pores.

[0034] The details of the heat exchanger tubes Nos. 4 and 5 are as follows.

Heat exchanger tube No. 4

[0035] Ceramics metal composite: Al+AlN of 90wt% or higher, thickness of 4mm, pore ratio of 20%, outer diameter of 40mm.

Heat exchanger tube No. 5

[0036] Ceramics metal composite: Al+AlN of 90wt% or higher, thickness of 6mm, pore ratio of 60%, outer diameter of 40mm

[0037] As a result, in each of the heat exchanger tubes, the ash containing basic salt was not piled on the surface. When steam of 150 to 400° C at the inlet was used as a heat exchanger fluid, it could be heated until the outlet temperature became 500° C, and when mixed gas of 120 to 300° C at the inlet of air of 1000 to 5000mmAq and combustion waste gas of 100 to 400mmAq was used, it could be heated until the outlet temperature became around 800° C, and the heat recovery could be done at high heat exchanger effectiveness.

[0038] In the case of the heat exchanger tube No. 5 of the pore ratio being 60%, if the pressure of heat exchanger fluid was strengthened to be 500mmAq or higher, the temperature around the outer surface of the heat exchanger tube went down by 100° C or higher than the temperature of the waste gas atmosphere. Therefore, the pressure of heat exchanger fluid is preferably determined to be about 400mmAq.

Example 3

[0039] There were installed for heat recovery, in the high temperature waste gas of 650 to 950° C of the municipal waste combustion pilot plant similar to Example 1, the heat exchanger tubes Nos. 6 to 9 having a vertically cross sectional shape shown in Fig. 4 and a laterally cross sectional shape shown in Fig. 5 where a heat resisting alloy tube 2 was covered with a ceramics metal composite 1 in non adhesive condition, and the heat resisting alloy tube 2 and the ceramics metal composite 1 at least partly contact at the interface therebetween, that

is, the spaces 5 existing.

[0040] The details of the heat exchanger tubes Nos. 6 to 9 are as follows.

Heat exchanger tube No. 6

[0041] Heat resisting alloy tube: SUS304-15A, Ceramics metal composite: Al+AlN+AlON of 90wt% or more, thickness of 5 to 10mm, pore ratio of 40%.

Heat exchanger tube No. 7

[0042] Heat resisting alloy tube: SUS304-20A, Ceramics metal composite: Al+AlN+AlON of 90wt% or more, thickness of 6 to 8mm, pore ratio of 20%

Heat exchanger tube No. 8

[0043] Heat resisting alloy tube: SUS304-20A, BN-coated, Ceramics metal composite: Al+AlN+AlON of 90wt% or more, thickness of 6 to 8mm, pore ratio of 20%.

Heat exchanger tube No. 9

[0044] Heat resisting alloy tube: SUS304-20A, Ceramics metal composite: Al₂O₃ of 80wt% or more+Al, thickness of 2 to 4mm, pore ratio of 30%.

[0045] The component of the waste gas of the municipal waste combustion pilot plant was O₂ of 2 to 16%, HCl of 200 to 600ppm, SOx of max 300ppm, CO₂ of 4 to 19% and the rest being N₂.

[0046] As a result, it was confirmed that in each of the heat exchanger tubes, the reduction amount of thickness by corrosion was slight, no crack occurred, and the stable heat recovery was possible for a long time. In particular, it was confirmed that no variations were recognized in the cross sectional shape after the tests in the heat exchanger tube No. 8 where BN was coated on the outer surface of the heat resisting alloy tube, and the sliding between the BN coating and the ceramics metal composite was smooth.

[0047] It was confirmed that when the heat exchanger fluid was steam of 300 to 400° C at the inlet, the outlet was 500° C or higher and 100ata, and when the heat exchanger fluid was mixed gas of air of 1000 to 5000mmAq and combustion waste gas of 100 to 400mmAq, it could be heated up to maximum of 800° C at the outlet.

Example 4

[0048] There were installed for heat recovery, in the high temperature waste gas of 700 to 1000° C of the municipal waste combustion pilot plant similar to Example 1, the heat exchanger tubes Nos. 10 and 11 having a vertically cross sectional shape shown in Fig. 4 and a laterally cross sectional shape shown in Fig. 5 where a

heat resisting alloy tube 2 was covered with a ceramics metal composite 1 in non adhesive condition, and the heat resisting alloy tube 2 and the ceramics metal composite 1 at least partly contact at the interface therebetween, that is, the spaces 5 existing.

[0049] The details of the heat exchanger tubes Nos. 10 and 11 are as follows.

Heat exchanger tube No. 10

[0050] Heat resisting alloy tube: Boiler heat resisting tube STBA28-20A, Ceramics metal composite: Al+AlN of 90wt% or more, Al₂O₃ of 7wt%, thickness of 6 to 7mm, pore ratio of 25%.

Heat exchanger tube No. 11

[0051] Heat resisting alloy tube: Boiler heat resisting tube STBA28-20A, Ceramics metal composite: SiC of 95wt% or more+Mg, thickness of 6 to 7mm, pore ratio of 2%.

[0052] As a result, since the high temperature waste gas included CO of 5 to 15%, there was scarcely deterioration due to oxidation of SiC or AlN, and the heat recovery was preferable.

Example 5

[0053] There were installed for heat recovery, in a combustion gas of a combustion furnace of coal, cakes of de-watered sewage and dried sewage, the heat exchanger tubes Nos. 12 to 14 where a heat resisting alloy tube 2 of coaxial shape or U-shape shown in Figs. 6 or 7 was covered with a ceramics metal composite 1 in non adhesive condition, and the heat resisting alloy tube 2 and the ceramics metal composite 1 at least partly contact at the interface therebetween, that is, the spaces 5 existing.

[0054] The details of the heat exchanger tubes Nos. 12 to 14 are as follows.

Heat exchanger tube No. 12

[0055] Heat resisting alloy tube: Boiler heat resisting tube STBA28-40A and 65A, Ceramics metal composite: SiC of 95wt% or more+Mg, thickness of about 7mm, Tube shape: coaxial(Fig. 6).

Heat exchanger tube No. 13

[0056] Heat resisting alloy tube: Boiler heat resisting tube STBA28-20A and 50A, Ceramics metal composite: Al₂O₃ of 95wt% or more+Al, thickness of about 3mm, Tube shape: coaxial(Fig. 6).

Heat exchanger tube No. 14

[0057] Heat resisting alloy tube: Boiler heat resisting

tube STBA28-15A and 20A, Ceramics metal composite: Al+AlN of 90 wt% or more, thickness of 6 to 10mm, Tube shape: U-shape(Fig. 7)

[0058] As a result, the combustion waste gas of coal and sewage contained SOx of several hundreds ppm, but no corrosion appeared in any of the heat exchanger tubes, and it was possible to recover steam of high temperature and high pressure, air of high temperature and waste gas of high temperature.

[0059] In the case of the U-shaped tube shown in Fig. 7, the turned part should have many spaces 5.

Example 6

[0060] There were installed for heat recovery, in the high temperature waste gas of 650 to 950°C of the municipal waste combustion pilot plant similar to Example 1, the heat exchanger tubes Nos. 15 to 18 having a vertically cross sectional shape shown in Fig. 8 and a laterally cross sectional shape shown in Fig. 9 where a heat resisting alloy tube 2 was covered in succession with a thermal expansion buffer 6 and a ceramics metal composite 1 in non adhesive condition, and both at least partly contact at the interface between the heat resisting alloy tube 2 and the thermal expansion buffer 6 and/or at the interface between the thermal expansion buffer 6 and the ceramics metal composite 1, that is, the spaces 5 existing.

[0061] The details of the heat exchanger tubes Nos. 15 to 18 are as follows.

Heat exchanger tube No. 15

[0062] Heat resisting alloy tube: SUS304-15A, Thermal expansion buffer: Al foil, thickness of 1 to 2mm, Ceramics metal composite: Al+AlN+AlON of 90wt% or more, thickness of 4 to 10mm, pore ratio of 40%.

Heat exchanger tube No. 16

[0063] Heat resisting alloy tube: SUS304-20A, Thermal expansion buffer: carbon fiber, thickness of 0.2 to 2mm, Ceramics metal composite: Al+AlN+AlON of 90wt% or more, thickness: 3 to 8mm, pore ratio of 20%.

Heat exchanger tube No. 17

[0064] Heat resisting alloy tube: SUS304-20A, BN-coated, Thermal expansion buffer: carbon fiber, thickness of 0.2 to 2mm, Ceramics metal composite: Al+AlN+AlON of 90wt% or more, thickness: 3 to 8mm, pore ratio of 20%

Heat exchanger tube No. 18

[0065] Heat resisting alloy tube: SUS304-20A, Thermal expansion buffer: carbon fiber, thickness of 1 to 2mm, Ceramics metal composite: Al₂O₃ of 80wt% or

more+Al, thickness of 2 to 4mm, pore ratio of 30%

[0066] The component of the waste gas of the municipal waste combustion pilot plant was O₂ of 2 to 16%, HCl of 200 to 600ppm, SOx of max 300ppm, CO₂ of 4 to 19% and the rest being N₂.

[0067] As a result, it was confirmed that in each of the heat exchanger tubes, the reduction amount of thickness by corrosion was slight, no crack occurred, and the stable heat recovery was possible for a long time. In particular, it was confirmed that no variations were recognized in the cross sectional shape after 1200 hours in the heat exchanger tube No. 17 where BN is coated on the outer surface of the heat resisting alloy tube, and the sliding between the BN coating and the ceramics metal composite was smooth.

[0068] It was confirmed that when the heat exchanger fluid was steam of 280 to 400° C at the inlet, the outlet was 540° C or higher and 100ata, and when the heat exchanger fluid was mixed gas of 120 to 300° C at the inlet of air of 1000 to 4000mmAq and combustion waste gas of 50 to 400mmAq, it could be heated up to maximum of 800° C at the outlet.

Example 7

[0069] There were installed for heat recovery, in the high temperature waste gas of 650 to 950°C of the municipal waste combustion pilot plant similar to Example 1, the heat exchanger tubes Nos. 19 and 20 having a vertically cross sectional shape shown in Fig. 8 and a laterally cross sectional shape shown in Fig. 9 where a heat resisting alloy tube 2 was covered in succession with a thermal expansion buffer 6 and a ceramics metal composite 1 in non adhesive condition, and both at least partly contact at the interface between the heat resisting alloy tube 2 and the thermal expansion buffer 6 and/or at the interface between the thermal expansion buffer 6 and the ceramics metal composite 1, that is, the spaces 5 existing.

[0070] The details of the heat exchanger tubes Nos. 19 and 20 are as follows.

Heat exchanger tube No. 19

[0071] Heat resisting alloy tube: Boiler heat resisting tube STBA28-20A, Thermal expansion buffer: fiber of carbon being 80wt% or more, thickness of 0.5 to 3mm, Ceramics metal composite: Al+AlN of 86wt% and Al₂O₃ of 6wt%, thickness of 4 to 5mm, pore ratio of 25%.

Heat exchanger tube No. 20

[0072] Heat resisting alloy tube: Boiler heat resisting tube STBA28-20A, Thermal expansion buffer: fiber of carbon being 80wt% or more, thickness of 1 to 3mm, Ceramics metal composite: SiC of 95wt% or more+Mg, thickness of 4 to 5mm, pore ratio of 2%.

[0073] As a result, since the high temperature waste

gas included CO of 5 to 15%, there was scarcely deterioration due to oxidation of SiC or AlN, and the heat recovery was preferable.

Example 8

[0074] There were installed for heat recovery, in the high temperature waste gas of 650 to 950°C of the municipal waste combustion pilot plant similar to Example 1, the heat exchanger tubes Nos. 21 to 23 where a heat resisting alloy tube 2 of coaxial shape or U-shape shown in Figs. 10 or 11 was covered in succession with a thermal expansion buffer 6 and a ceramics metal composite 1 in non adhesive condition, and both at least partly contact at the interface between the heat resisting alloy tube 2 and the thermal expansion buffer 6 and/or at the interface between the thermal expansion buffer 6 and the ceramics metal composite 1, that is, the spaces 5 existing.

[0075] The details of the heat exchanger tubes Nos. 21 and 23 are as follows.

Heat exchanger tube No. 21

[0076] Heat resisting alloy tube: Boiler heat resisting tube STBA28-40A and 65A, Thermal expansion buffer: mixture of powder of carbon being 80wt% or more and fiber, thickness of 0.2 to 4mm, Ceramics metal composite: SiC of 95wt% or more+Mg, thickness of 7mm, Tube shape: coaxial(Fig. 10).

Heat exchanger tube No. 22

[0077] Heat resisting alloy tube: Boiler heat resisting tube STBA28-20A and 50A, Thermal expansion buffer: carbon being 80wt% or more, thickness of 0.3 to 2mm, Ceramics metal composite: Al₂O₃ of 95wt% or more+Al, thickness of about 4mm, Tube shape: coaxial(Fig. 10).

Heat exchanger tube No. 23

[0078] Heat resisting alloy tube: Boiler heat resisting tube STBA28-15A and 20A, Thermal expansion buffer: fiber of carbon being 80wt% or more, thickness of 0.4 to 1mm, Ceramics metal composite: Al+AlN of 90wt% or more, thickness of 6 to 8mm, Tube shape: U-shape (Fig. 11).

[0079] As a result, the combustion waste gas of coal and sewage contained SOx of several hundreds ppm, but no corrosion appeared in any of the heat exchanger tubes, and it was possible to recover steam of high temperature and high pressure, air of high temperature and waste gas of high temperature.

[0080] In the case of the U-shaped tube, the turned part should have many spaces 5.

Claims

1. A heat exchanger tube made of a sintered compact having pore ratio of 2 to 60%.
2. The heat exchanger tube of Claim 1, wherein the sintered compact is made of a ceramics metal composite.
3. A heat recovery method, using the heat exchanger tube of Claim 1, and comprising a step of strengthening the pressure of heat exchanger fluid passing within the heat exchanger tube than the pressure of an atmosphere outside of the heat exchanger tube.
4. A heat recovery method, using the heat exchanger tube of Claim 2, and comprising a step of strengthening the pressure of heat exchanger fluid passing within the heat exchanger tube than the pressure of an atmosphere outside of the heat exchanger tube.
5. A heat exchanger tube, wherein the outer part thereof is made of a ceramics metal composite.
6. The heat exchanger tube of Claim 5, wherein the ceramics metal composite contains AlN of 1 to 90wt% and Al+AlN of 50wt% or more.
7. The heat exchanger tube of Claim 5, wherein the ceramics metal composite contains AlN of 1 to 90wt% and Al+AlN+AlON of 50wt% or more.
8. The heat exchanger tube of Claim 5, wherein a compound containing B(boron) or C(carbon) exists in the outer surface of the ceramics metal composite.
9. The heat exchanger tube of Claim 5, wherein the thickness of the ceramics metal composite is 3 to 12mm.
10. A heat exchanger tube, wherein a heat resisting alloy tube is covered with a ceramics metal composite in non adhesive condition, and the heat resisting alloy tube and the composite at least partly contact at the interface therebetween.
11. The heat exchanger tube of Claim 10, wherein the ceramics metal composite contains AlN of 1 to 90wt% and Al+AlN+AlON of 50wt% or more.
12. The heat exchanger tube of Claim 10, wherein a compound containing B or C exists in the outer surface of the heat resisting alloy tube.
13. The heat exchanger tube of Claim 10, wherein the ceramics metal composite has pore ratio of 2 to 60%.

14. A heat exchanger tube, wherein a heat resisting alloy tube is covered in succession with a thermal expansion buffer and a ceramics metal composite in non adhesive condition, and both at least partly contact at the interface between the heat resisting alloy tube and the thermal expansion buffer and/or at the interface between the thermal expansion buffer and the ceramics metal composite. 5
15. The heat exchanger tube of Claim 14, wherein the ceramics metal composite contains AlN of 1 to 90wt% and Al+AlN+AlON of 50wt% or more. 10
16. The heat exchanger tube of Claim 14, wherein the thermal expansion buffer is a fiber, powder, film, tape and the like containing B, C or Al as a main component. 15
17. The heat exchanger tube of Claim 14, wherein a compound containing B or C exists in the outer surface of the heat resisting alloy tube. 20
18. The heat exchanger tube of Claim 14, wherein the ceramics metal composite has pore ratio of 2 to 60%. 25

30

35

40

45

50

55

FIG. 1

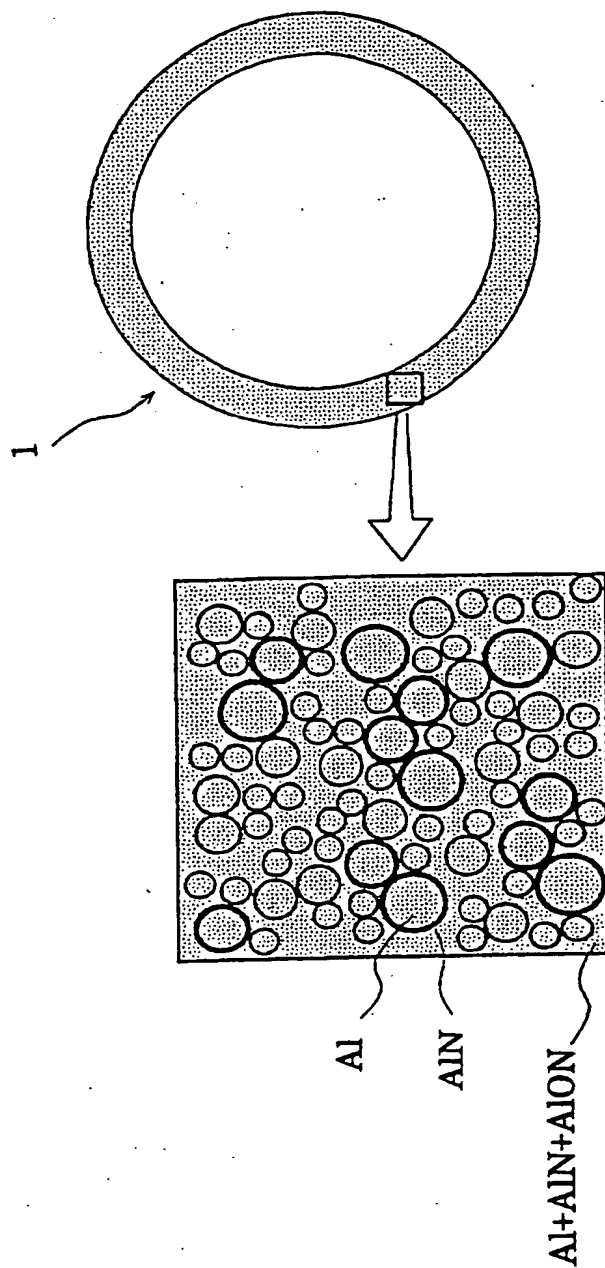


FIG. 2

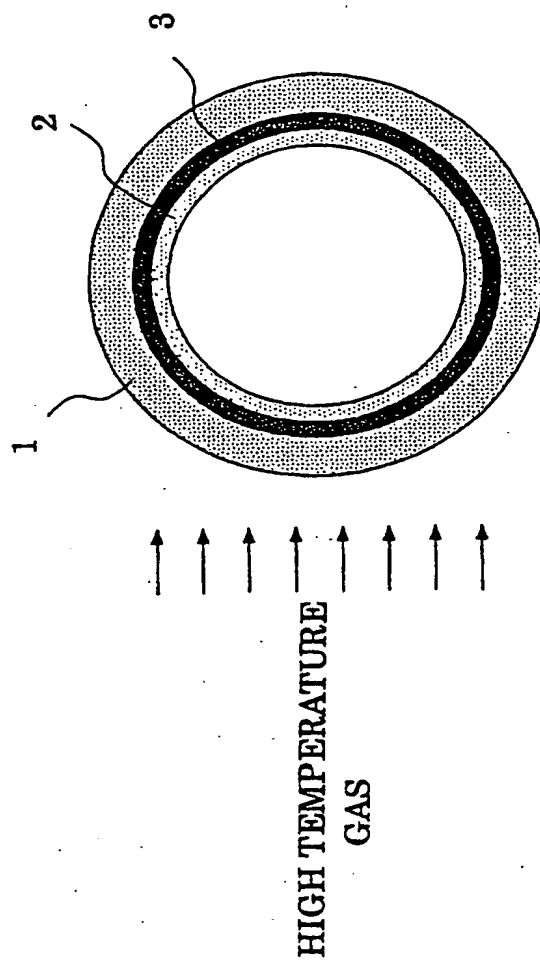


FIG. 3

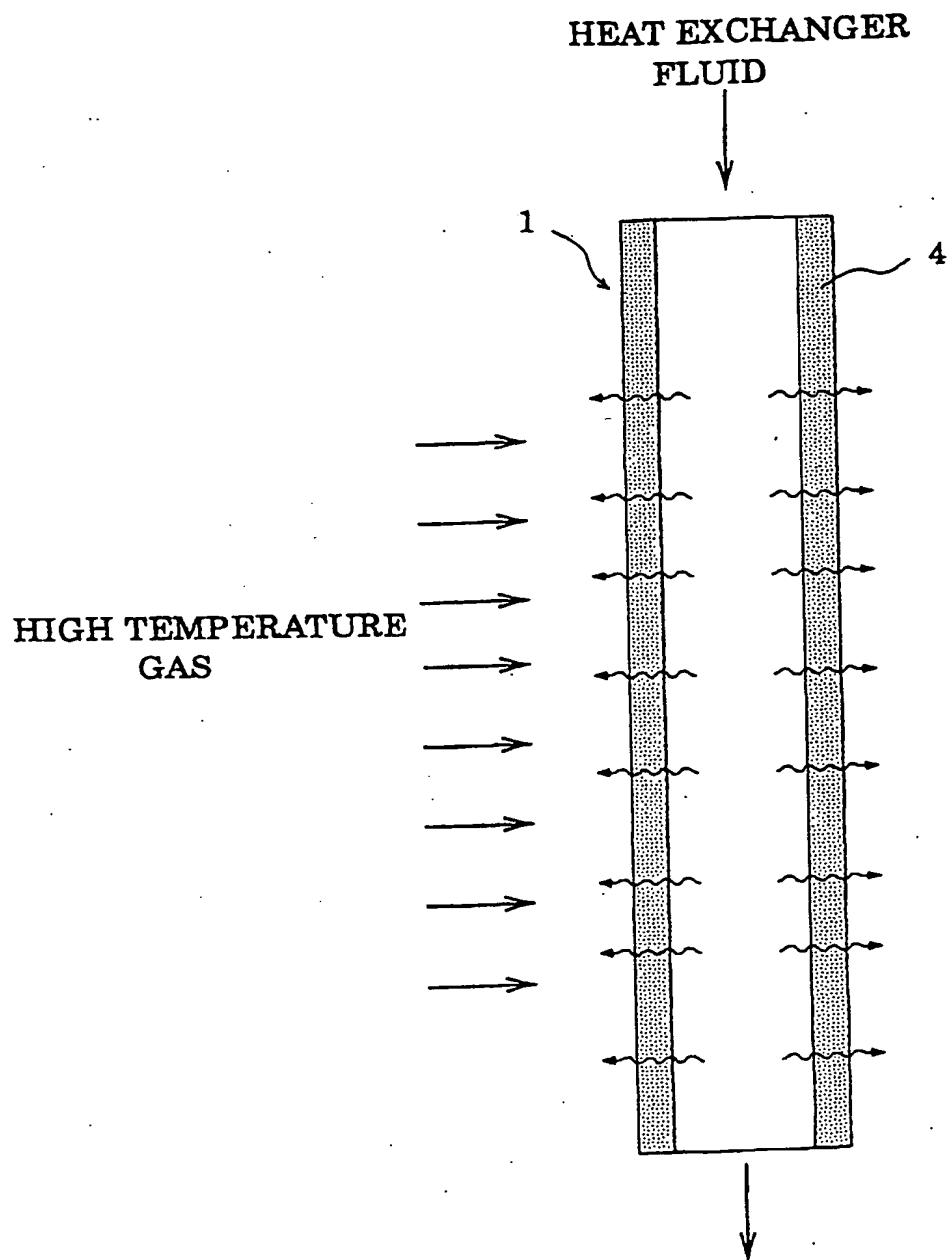


FIG. 4

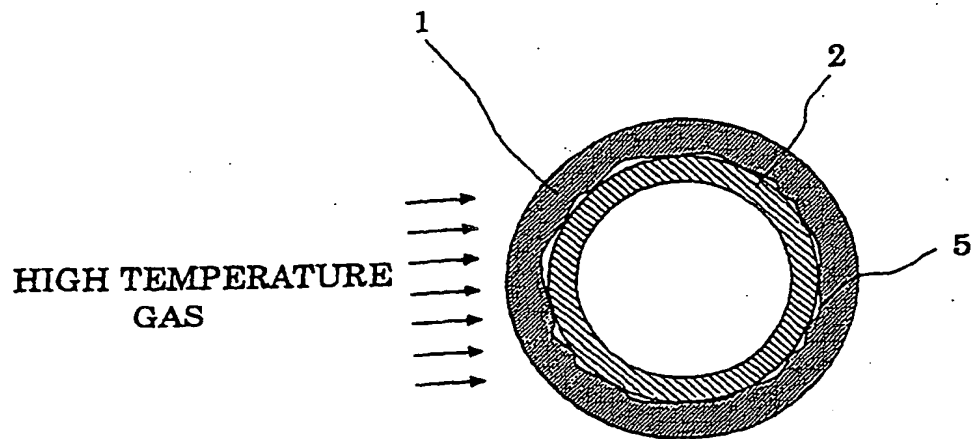


FIG. 5

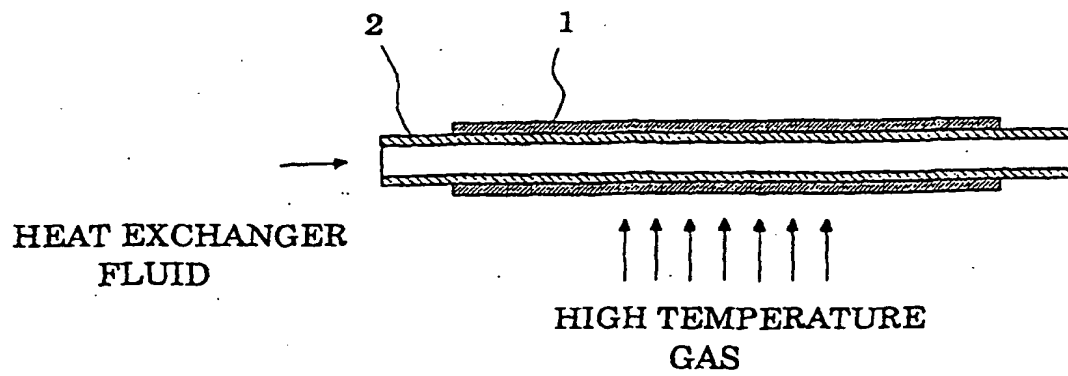


FIG. 6

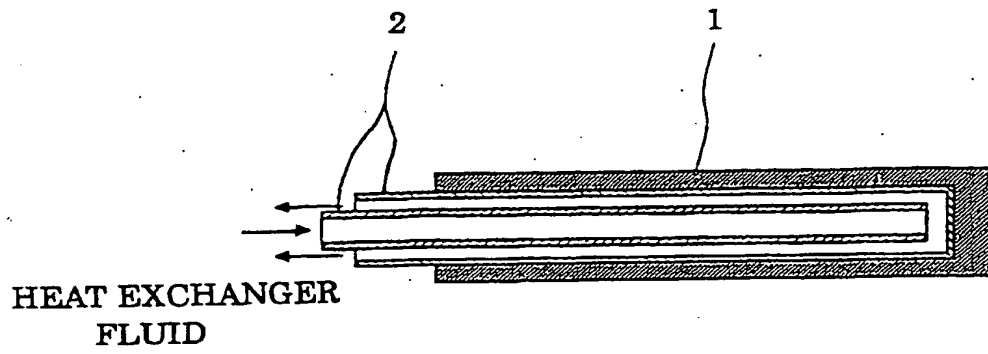


FIG. 7

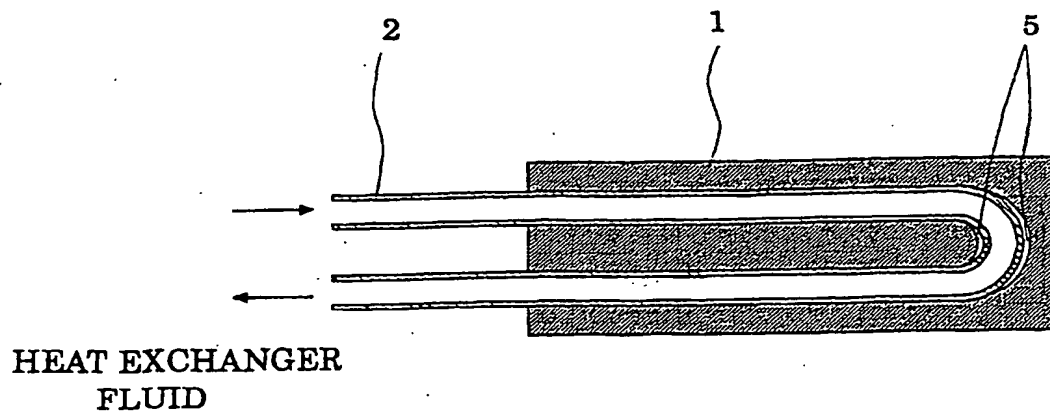


FIG. 8

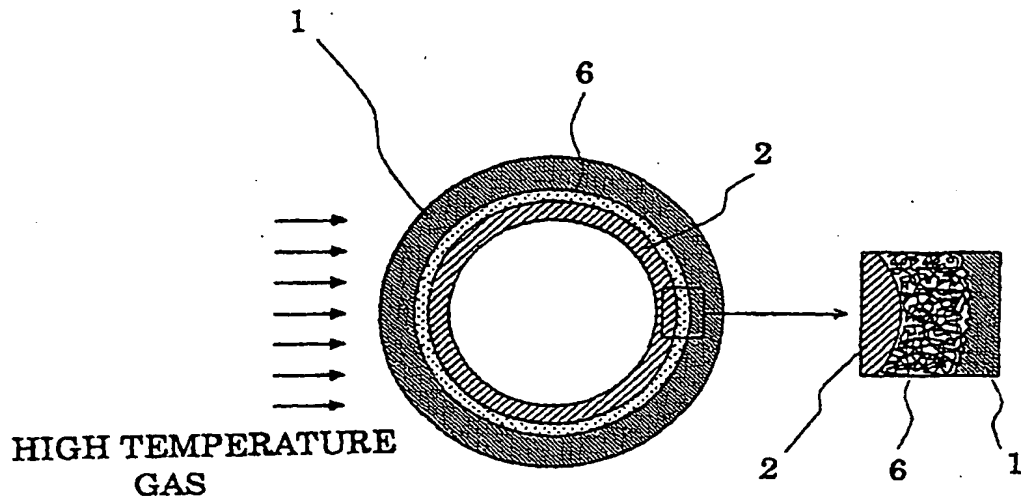


FIG. 9

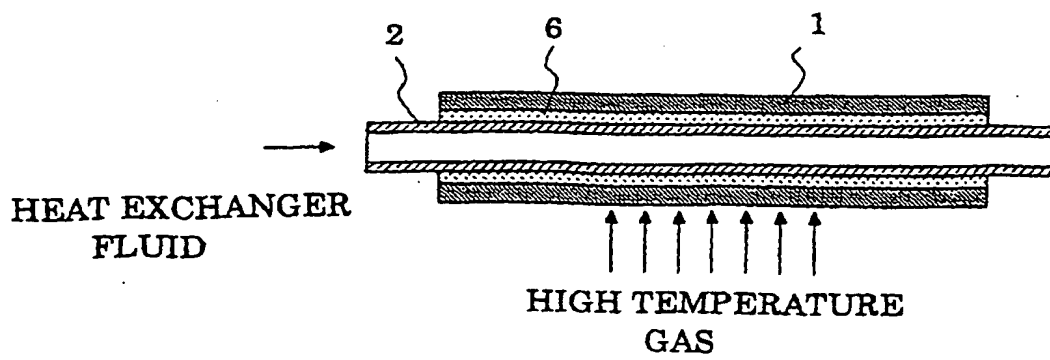


FIG. 10

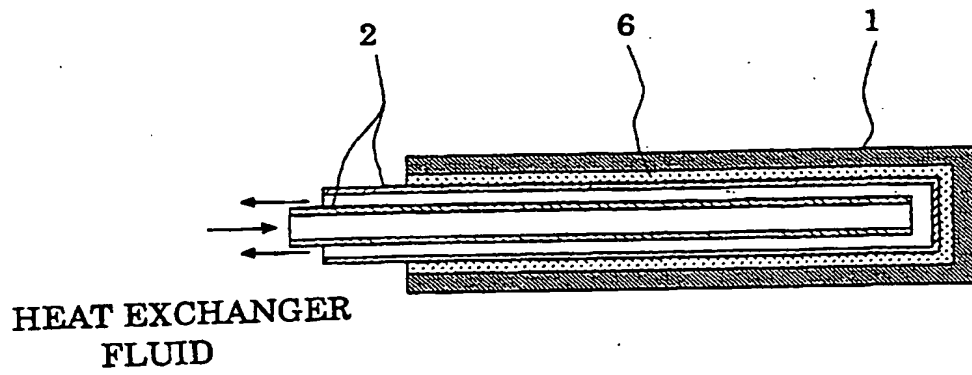
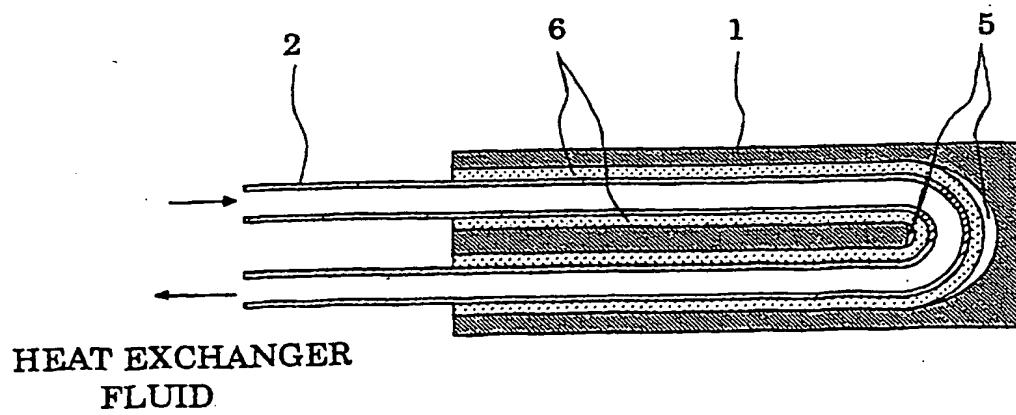


FIG. 11



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP00/05205

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl.⁷ F28F19/02, 21/00, 21/04, 21/08, 1/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl.⁷ F28F19/00-19/06, F28F21/00-21/08, 1/12

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1926-1996	Toroku Jitsuyo Shinan Koho	1994-2000
Kokai Jitsuyo Shinan Koho	1971-2000	Jitsuyo Shinan Toroku Koho	1996-2000

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, 61-83895, A (Hitachi, Ltd.), 28 April, 1986 (28.04.86), Full text (Family: none)	1-4
Y	JP, 6-307791, A (YKK Corporation), 01 November, 1994 (01.11.94), Full text (Family: none)	1-4
A	JP, 5-180585, A (INR Kenkyusho K.K.), 23 July, 1993 (23.07.93), Full text (Family: none)	1-4
Y	JP, 1-159596, A (Toshiba Corporation), 22 June, 1989 (22.06.89), Full text (Family: none)	1-18
Y	JP, 4-371800, A (Yoshida Kogyo K.K.), 24 December, 1992 (24.12.92), Full text (Family: none)	1-18
Y	JP, 61-227036, A (Mitsubishi Heavy Industries, Ltd.), 09 October, 1986 (09.10.86), Full text	1-18

☒ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search
22 September, 2000 (22.09.00)Date of mailing of the international search report
03 October, 2000 (03.10.00)Name and mailing address of the ISA/
Japanese Patent Office

Authorized officer

Facsimile No.

Telephone No.

EP 1 122 506 A1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP00/05205

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	(Family: none) JP, 63-140292, A (Chuo Denki Kogyo K.K.), 11 June, 1988 (11.06.88), Full text (Family: none)	1-18

Form PCT/ISA/210 (continuation of second sheet) (July 1992)